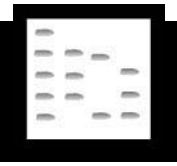
ATMOSPHERIC ANALYSIS: GAS CHROMATOGRAPHY



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Introduction

The determination of both naturally produced and anthropogenic organic species in the atmosphere is a key area in atmospheric chemistry research. Nearest to the earth's surface, within the boundary layer of the troposphere, the determination of hydrocarbon species is important because of their ability to react rapidly with NO_x in the presence of sunlight to form photochemical smog. At the other extreme of the atmosphere in the stratosphere, remote measurements of very long-lived halogenated species are required because of their critical impact on ozone destruction. Species such as methane, present throughout the atmosphere, have importance as greenhouse gases and influence global climate and temperature change.

The wide range of both short- and long-lived species that are of interest in atmospheric science coupled to extremely low concentrations and a requirement often for *in situ* automated analysis has led to the development of many novel chromatographic techniques and methodologies. While some atmospheric species such as organic acids, peroxides and aldehydes have been determined using high performance liquid chromatography, the majority of species are analysed using capillary gas chromatography. The range of compounds that are of interest has resulted in almost every kind of detector finding a role within atmospheric analysis.

This article only deals with the analysis of species found in the gas phase, although many species present in the atmosphere are bound to particles or are in aerosol form. A vast number of methodologies for analysis of these species exist, although in common with gas phase species, gas chromatography plays a vital role in their analysis.

The range of techniques that are in use is so broad that a complete review of analytical methods is impractical. Many individual methods, however, have common components or key procedural steps and these will be discussed. A general outline of a typical atmospheric determination can be broken down into the following steps: sample acquisition, preparation, separation and detection. The first two stages, acquisition and preparation, often prove to be the most challenging. A number of chromatograms obtained from atmospheric analysis are also presented in **Figures 1–4**. **Figures 1** and **2** were obtained from an urban environment and **Figures 3** and **4** came from a single field campaign held on the west coast of Ireland to study clean marine air.

Sample Acquisition

The initial step of sample acquisition is a far from trivial task in atmospheric measurements, and segregates a major grouping of techniques into either *in situ* or post-acquisition analysis. The ability to store an atmospheric sample is critical to the decision on whether analysis may be performed back in the laboratory or on-site immediately following acquisition. Stable species such as methane, carbon monoxide and chlorinated fluorocarbons may be stored successfully in sample vessels for many weeks without affecting sample integrity, and widespread measurements of these species have therefore been performed. Atmospheric degradation products, such as peroxyacetyl nitrate (PAN, $CH_3C(O)_2ONO_2$), are so unstable, however, that analysis must be performed immediately. For many other important reactive species such as alkenes, monoterpenes and dimethyl sulphide, the storage of samples has been shown to lead to a degree of analyte losses due to reaction with co-sampled pollutants such as ozone and oxides of nitrogen. To overcome these problems of reaction during storage, many forms of scrubber (e.g. potassium iodide and glycerol to remove ozone) have been tested to remove such species without affecting sample integrity.

Much atmospheric sampling is performed using canister methods, filled either by vacuum release or by pumping sample into the canister using stainless steel or Teflon diaphragm pumps. For any sample to be stored successfully there must be minimal interaction with the canister walls and coating methods such as electropolishing, silica or Teflon coating are currently in use. The preparation and cleaning of canisters require careful attention and high vacuums are often applied together with elevated temperatures for periods of hours or even days. A similar method to canister samples is the use of collapsible Teflon or Tedlar sample bags. These bags may be filled by pump and returned to a laboratory for analysis using very similar procedures to those used with canister

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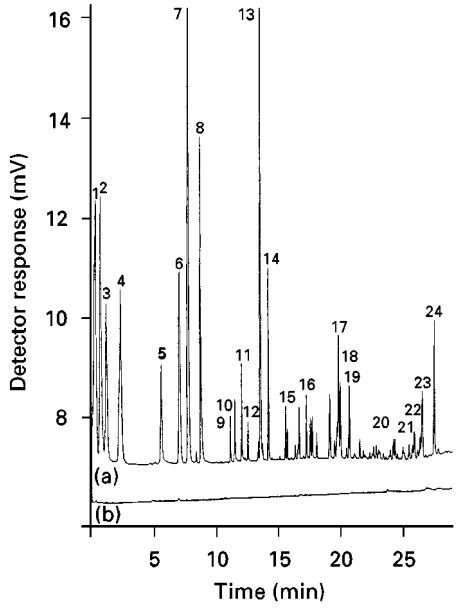

Figure 1 Low molecular weight hydrocarbons including methane determined using an online activated charcoal adsorbent trap in a programmed temperature vaporization injector. Column 50 m, 0.53 mm i.d. $Al_2O_3/NaSO_4$ PLOT (Chrompack) 10 μm film thickness. Desorption temperature was at 16°C s^{-1} from −20°C to 400°C, and column temperature programmed from 45°C to 200°C. Chromatograms showing (a) the separation of C_1–C_6 components of Leeds city-centre air, and (b) a blank following desorption. Peaks: 1 = methane, 2 = ethane, 3 = ethene, 4 = propane, 5 = propene, 6 = 2-methylpropane, 7 = ethyne, 8 = *n*-butane, 9 = *trans*-2-butene, 10 = 1-butene, 11 = isobutene, 12 = *cis*-2-butene, 13 = 2-methylbutane, 14 = *n*-pentane, 15 = 1,3-butadiene, 16 = pentenes, 17 = 2-methylpentane, 18 = 3-methylpentane, 19 = *n*-hexane, 20 = methyl hexanes and hexenes, 21 = heptane, 22 = methylcyclopentane, 23 = benzene, 24 = toluene. Reproduced with permission from Lewis AC and Bartle KD 1996. A simplified method for the determination of atmospheric hydrocarbons. *LC–GC International* 9: 297–304.

samples. While generally of lower unit cost, the bag method often produces a greater degree of sample artefact and analyte losses.

Some low volatility species are less suitable for sampling using canister methods because of the increased possibility of analyte condensation on to the walls of the container. For this reason a second method of sample acquisition is widely used based on use of a solid-phase adsorbent as an analyte trap. The adsorbent used in the trap may be chosen to introduce an element of selectivity to the trapping mechanism, although in practice a trap-all approach is commonly used. Adsorbent traps allow for instrument automation that is not always possible with canister methods and such traps now form the basis of many national monitoring programmes in the urban environment, as well as automated instruments for research in very clean air.

A huge range of adsorbents is currently available from high surface area ($>1000\,m^3\,g^{-1}$) carbon-based materials with strong retention characteristics to lower surface area ($<50\,m^3\,g^{-1}$) polymers such as Tenax TA. While being relatively low cost compared to sample canisters, care is often required in the cleaning and preparation of sample tubes. Samples may be introduced to the adsorbent tubes either dynamically over short periods of time (typically minutes) or via diffusional sampling over longer periods (typically several days). Carbon-based adsorbents are suitable for a wide range of species ranging from volatile hydrocarbons and CFCs to organic nitrates. Polymeric materials are used mainly for the concentration of low volatility species such as aromatics and monoterpenes in air, although compounds as large as two and three ring polycyclic aromatics may also be successfully trapped and desorbed from the gas phase.

Sulfur species trapping is often performed via chemisorption on to gold wool traps that provide a stable matrix for the sample to be stored for reasonable periods of time.

The complete retention of all target analytes on the adsorbent bed must be carefully evaluated and calculation of retention volume (often referred to as breakthrough volume) is essential. For sampling very volatile species (for example ethane or ethene) the retention volume for an adsorbent system is often the critical factor in determining system sensitivity. Trapping at sub-ambient temperatures is commonly employed to increase the maximum sample volume, often using liquid nitrogen or carbon dioxide. For operation of any instrument in a field location, the supply of these coolants may be a problem and modern instruments often now employ Peltier coolers.

Sample Preparation and Injection

Removal of Water

The inevitable presence of water in atmospheric samples and its removal prior to sample analysis is a complex area. In certain circumstances its presence may be both beneficial, e.g. with canister samples where it occupies the active sites on the canister walls, or detrimental, e.g. where it affects analysis in some way. Alumina porous layer open tubular (PLOT) columns are particularly affected by moisture in the sample, and large changes in stationary phase affinity occur when water is introduced. Detectors such as mass spectrometers are also extremely sensitive to water introduced with the sample and high background noise may result. Even the flame

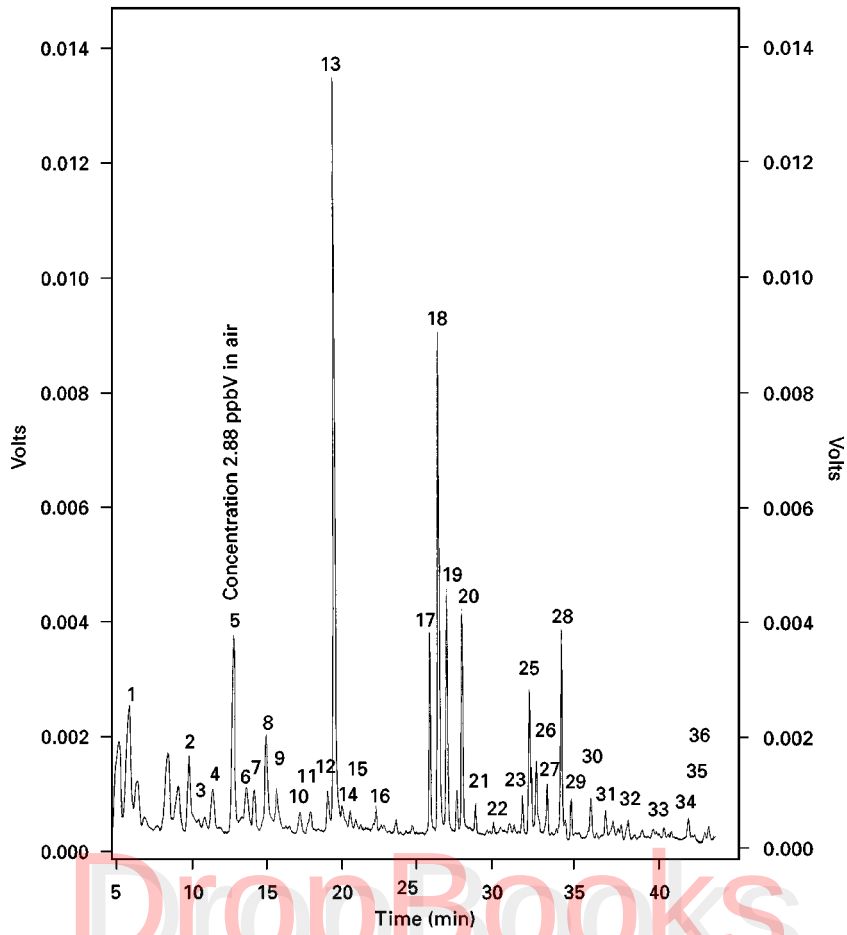

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Figure 2 Aromatic hydrocarbon species determined using an online Tenax TA adsorbent trap in a programmed temperature vaporization injector. Column 60 m, 0.53 mm i.d., poly(dimethylsiloxane) 3 μm film thickness. (Restek RTX-1). Desorption temperature was at 16°C s^{-1} from 0°C to 220°C, and column temperature programmed from 35°C to 240°C.

1. unresolved volatile material
2. hexane
3. methyl cyclopentane
4. 2,4-dimethylpentane
5. benzene
6. 2-methylhexane
7. 3-methylhexane
8. 2,2,4-trimethylpentane
9. heptane
10. methyl cyclohexane
11. 2,4- and 2,5-dimethylhexane
12. 2,2,3-trimethylpentane
13. toluene
14. 2- and 4-methylheptane
15. 3-methylheptane
16. octane
17. ethylbenzene
18. *m*- and *p*-xylene
19. styrene
20. *o*-xylene
21. nonane
22. isopropylbenzene
23. propylbenzene
24. *m*-ethyltoluene
25. *p*-ethyltoluene
26. 1,3,5-trimethylbenzene
27. *o*-ethyltoluene
28. 1,2,4-trimethylbenzene
29. decane
30. 1,2,3-trimethylbenzene
31. indane
32. 1,4-dimethyl 2-ethylbenzene
33. dimethylethylbenzenes and undecane
34. 1,2,3,5-tetramethylbenzene
35. naphthalene
36. dodecane

(Reproduced with permission from Lewis AC *et al.* (1996) Atmospheric monitoring of volatile organic compounds using programmed temperature vaporisation injection. *Journal of High Resolution Chromatography* 19: 686–690.)

ionization detector can be affected by injection of water, and the flame may be extinguished when water elutes from the column.

Many forms of selective water removal exist, the simplest of which is the use of condensation traps or stripping coils. Losses of low boiling molecular species are insignificant although condensation of higher boiling organic material may arise at low condensation temperatures. Inorganic adsorbents are also commonly used, notably potassium carbonate and magnesium perchlorate. Adsorbents such as these, however, have limited capacity and often require frequent regeneration or replacement. A combination of initial condensation and second stage adsorbent scrubber often provides sufficient capacity to dry a sample stream of air for many hours or days. Con-

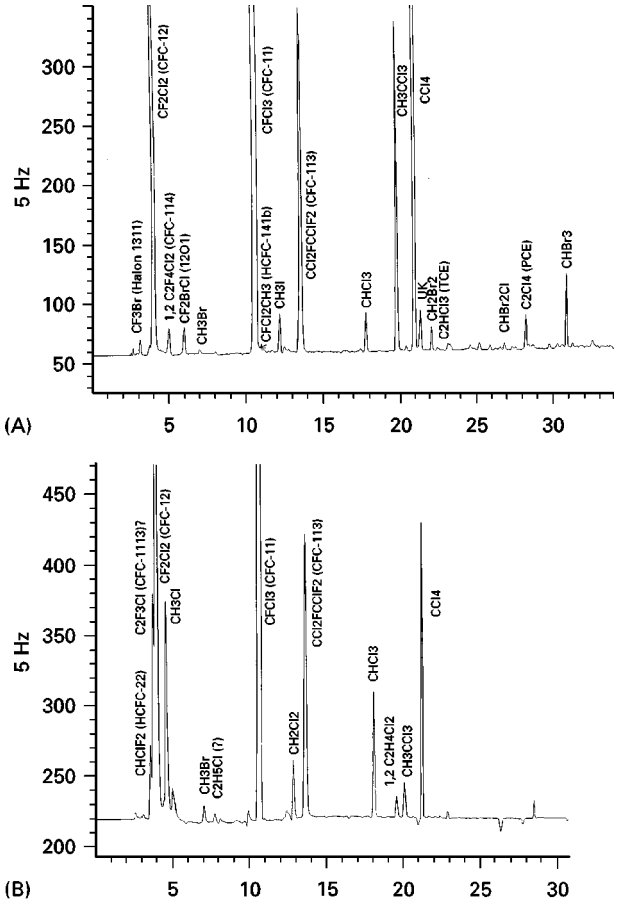

Figure 3 CFCs and halon species in clean marine air determined using an online Carbosieve micro adsorbent trap and direct injection to capillary GC. Detection by dual ECD/oxygen-doped ECD. Column 60 m, 0.33 mm i.d., 1 μm film DB-1 (J&W). (A) Stage 1: standard ECD; (B) Stage 2: oxygen-doped ECD. (Reproduced with permission from Bassford M, and Simmonds PG, University of Bristol, Cantocks Place, Bristol.)

tinuous drying may be achieved using permeation membranes such as Nafion. These forms of driers operate by means of a concentration gradient across a membrane that is permeable only to highly polar material such as water. A counter-current of dry gas is passed around the outside of the membrane as a sheath gas and carries moisture away to waste. However, this type of drier is unsuitable for samples where the quantitation of polar materials is required.

Direct loop injection High concentration atmospheric species require the least amount of sample preparation, often only the removal of excess water from the sample. Methane, carbon monoxide and N_2O analyses are performed simply by filling a known volume injection loop, followed by direct injection into the analytical column. Backflushing is often then performed to remove the remaining components from the analytical column. A further example of direct loop injection is in the analysis of PAN where, due to thermal decomposition of the sample, analysis must be performed *in situ*. It is performed using direct loop injection to a cooled isothermal pre-column followed by a short analytical capillary column coupled to an electron capture detector. An ancillary measurement of carbon tetrachloride is often gained from using this approach.

Sample concentration methods Whether an atmospheric sample is collected using adsorbent or canister techniques, several stages of sample preparation are required prior to injection into the analytical column. The sheer size of sample – often many litres – precludes any form of direct injection except in the case of the high concentration species described earlier, making sample concentration a vital step prior to injection.

Canister samples require complete concentration prior to introduction to the capillary column.

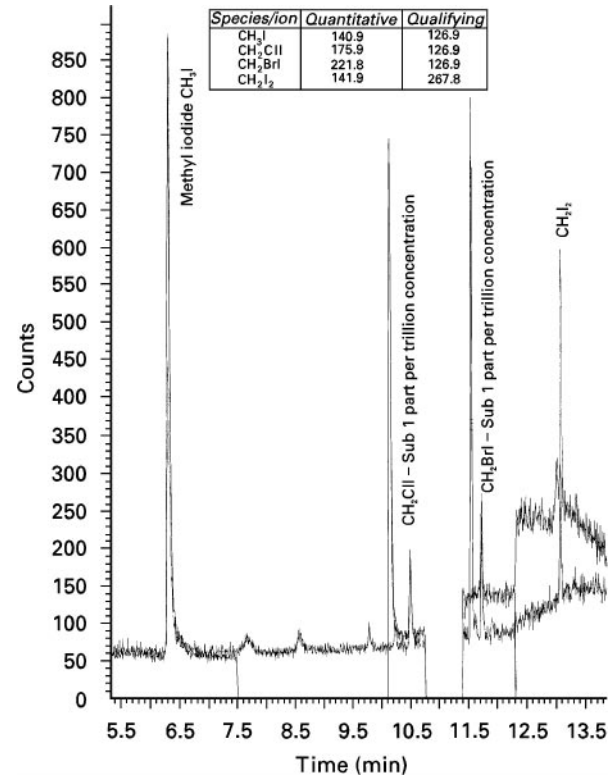
Species/ion | Quantitative | Qualifying
CH3I | 140.9 | 126.9
CH2ClI | 175.9 | 126.9
CH2BrI | 221.8 | 126.9
CH2I2 | 141.9 | 267.8
Methyl iodide CH3I
CH2ClI – Sub 1 part per trillion concentration
CH2BrI – Sub 1 part per trillion concentration
CH2I2
Counts
Time (min)

Figure 4 GC–SIM/MS of natural halocarbons (CH_3I, CH_2ClI, CH_2BrI and CH_2I_2) in marine air. PLOT column trap cooled with liquid nitrogen. Flash heating to capillary GC. Column 60 m, 0.33 mm i.d., 1.8 μm film DB-VRX (J&W). Detection by single ion monitoring HP mass selective detector. (Reproduced with permission from Carpenter, L and Sturges, WT, School of Environmental Sciences, University of East Anglia, Norwich, UK.)

Analytes are removed from the canister via either internal canister pressure (for pumped-in samples) or vacuum pump (for atmospheric pressure samples) over a cryogenic trap. Liquid nitrogen is most commonly used but liquid argon has been used to reduce the amount of oxygen retained in the focusing stage. The concentration zone may consist of a packed tube containing either an absorbent such as Tenax TA or glass beads or it may simply be empty stainless steel tubing. Since the concentration stage is at such low temperatures, the majority of water vapour in the sample must be removed prior to focusing in order to stop blockage of lines with ice. Once a sufficient volume has been collected on the focusing trap, the trap is generally flash heated either electrically or by using hot water. This results in a very sharp band of compounds being introduced to the head of the analytical column.

With adsorbent tube analysis the collected analytes are generally thermally desorbed either directly on to the analytical column (in the case of programmed temperature vaporization injection), or on to a focusing cold trap. The desorption temperature is generally defined by the maximum temperature that the adsorbing material can support. For polymeric adsorbents this may be relatively low ($< 250^{\circ}C$) while carbon-based materials may support desorption at temperatures of 500°C or higher.

If a programmed temperature vaporization (PTV) injector is used, the desorption may be sufficiently rapid ($> 15^{\circ}C\,s^{-1}$) so that initial column focusing is sufficient to obtain well-resolved peaks. If the desorption from an adsorbent tube is relatively slow then a focusing step is used, with a similar concentration mechanism to that used with canister samples. Once again, water must be removed from the sample since it may affect the column or the detection system.

While the majority of species are thermally desorbed from the trap to the analytical column, a few types of compounds require solvent extraction prior to syringe injection. Organic nitrates fall into this class along with higher molecular weight polycyclic aromatic compounds that may suffer from incomplete or slow thermal release.

Separation of Atmospheric Samples

While a number of specific applications utilize packed columns (notably in the analysis of methane, CO and N_2O), current methods for the separation of atmospheric components are performed almost exclusively using capillary column gas chromatography.

The few applications remaining where packed columns are in use, generally employ molecular sieve packings for the separation of permanent gas species. With the introduction of Al_2O_3 PLOT columns, fast high resolution analysis of even the highest volatility species has been made possible and many applications that previously used packed column GC are now being performed using capillary columns.

Where only one species is to be determined simple isothermal separations may be used, often in conjunction with a column backflush step. The analysis of PAN is an example of this where a short backflushing pre-column is used prior to a 10 m analytical column. A simple two-dimensional separation has also been proposed for PAN using heart-cutting.

The wide magnitude of analyte volatilities encountered imposes limits on the range of species that can be successfully separated on a given column. PLOT columns are used widely for the analysis of C_1–C_7 hydrocarbons and some high volatility halogenated compounds. The retention characteristics of this type of column are not favourable for the analysis of oxygenated compounds, and water often plays a significant role in degrading the quality of any PLOT column separation. Very strong retention of higher boiling species leads to extensive peak broadening coupled with lengthy analysis times.

Analysis of higher molecular weight species, including volatile organic compounds (VOCs), CFCs and hydrogen-containing chlorofluorocarbon replacements (hCFCs), aromatic and monoterpene compounds, has commonly been performed with nonpolar (methylpolysiloxane) or slightly polar (5% phenyl methylpolysiloxane) 1–5 μm-thick film capillary columns, 0.32 mm i.d. by 50 m long. Wide bore, 0.53 mm i.d. columns are often used where desorption is direct from a preconcentration trap to the analytical column. For the analysis of complex hCFC mixtures in the atmosphere, columns as long as 100 m have been reported.

To improve retention of volatile VOCs on thick film siloxane columns, without use of sub-ambient cooling, operation with columns containing films up to 15 μm thick have been reported. Band broadening effects through stationary phase diffusion become significant with films of this thickness and this approach has not been widely adopted. The highest molecular weight gas phase species such as naphthalene, fluorene and anthracene may be separated efficiently only on thinner film non-polar columns with film thicknesses of typically 0.25–0.5 μm.

Organic nitrate species in the atmosphere may also be determined using capillary GC with either charcoal adsorbent traps, extracted with aromatic organic solvent or via direct cryofocusing from a canister sample. Lengthy analysis times can result due to the necessity of using combinations of columns to achieve full separation of target analytes although commonly

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moderate polarity 50% phenyl/50% methyl polysiloxane columns are used.

Detection Systems

Even the highest resolution capillary columns often have insufficient peak capacity to resolve all components in a typical atmospheric sample. Since selectivity in trapping is not always possible, selectivity in detection is a useful tool in the simplification of atmospheric analysis.

The flame ionization detector (FID) is by far the most commonly used detector in atmospheric analysis by GC since it offers high sensitivity, extremely wide linearity and good reliability. Using well-cleaned fuel gases coupled to low noise electrometer circuitry it is possible to determine amounts down to 1 pg s^{-1}. With a typical sample volume of 1 L, detection limits for individual species may be in the low parts per trillion range (10^{-12}). Calibration can be performed with relative ease but the complexity of samples can make peak identification difficult. Methods for alkene/aromatic analysis utilizing selective response from the photoionization detector (PID) have been proposed although they are not in widespread use.

Mass spectrometry offers obvious solutions to problems of compound identification but the operation of currently available bench-top MS in full scan mode often has insufficient sensitivity for trace level measurements. Spectral information obtained from GC/MS of atmospheric hydrocarbons often leads to highly similar fragmentation patterns and assists little in the identification of isomeric species. Similarly, identification of monoterpene species can only be confirmed through a combination of both spectral information and retention time data.

While MS of hydrocarbon species in clean air is often unsuccessful when operating in full scan mode there is sufficient sensitivity and resolution to allow for detection of long-lived CFC species. Long-term monitoring of these species has been performed by GC–ion trap detection in the worldwide MS–GAGE (global atmospheric gases experiment) network. In single ion mode, femtogram sensitivities can be achieved and this approach has been used for field monitoring of naturally produced trace level iodo- and bromo- compounds.

More commonly used for CFC measurements in the atmosphere is the electron-capture detector (ECD) that offers high sensitivity to certain species plus high selectivity over hydrocarbon compounds. GC–ECD measurements require careful calibration due to the great variation in response to halogenated species, although their high stability allows gas standards to be used over many years. Some halogen-containing species of interest (e.g. CH_3Cl, CHF_2Cl, CH_2Cl_2) have a relatively poor ECD response and the use of the oxygen-doped ECD to enhance their response has been successful and is demonstrated in Figure 3. The determination of some nitrogen-containing species is also performed using ECD, notably in the areas of organic nitrate analysis and the determination of PAN. Organic nitrate analysis using ECD is often complicated by the co-elution of halogenated compounds, so often a nitrogen-specific detector such as the chemiluminescence detector is used in parallel.

Detection of CO is generally performed using the reduction gas detector (RGD) where hot HgO reduction with one CO molecule releases one Hg molecule from a catalytic bed. The Hg molecule released is then detected by UV absorption.

The analysis of sulfur compounds in the atmosphere, in particular dimethyl sulfide (DMS), has often been performed using a combination of GC with sulfur selective detection to overcome problems of insufficient chromatographic resolution. Flame photometric detection (FPD) has been used extensively in the past although signal quenching by co-eluting hydrocarbons results in drastically reduced sensitivity. The *Hall* detector or electrolytic conductivity detector (ELCD) has also been used for atmospheric determinations although it requires regular maintenance making it unattractive for an automated instrument. Emerging methods are now taking advantage of significant advances in bench-top atomic emission detectors (AED). The multielemental nature of the AED offers significant advantages in atmospheric measurements both in terms of sensitivity (sulfur – 2 pg s^{-1}), and where concurrent emission line measurements for carbon and hydrogen may provide information on empirical formulae of unknown species. The sulfur chemiluminescence detector, which is a more recent technique that offers extremely high sensitivity and selectivity, may yet find an important role in atmospheric sulfur analysis.

The analysis of oxygenated species in the atmosphere is one of the least studied areas using gas chromatography. It is an area of fundamental significance where species may be present in the atmosphere as direct emissions or as degradation products of olefins. While most aldehydes and ketones may be successfully separated using GC, sample preparation and analyte detection are the key problem areas. Sample preparation is an area where new adsorbents may provide selective concentration of polar species simplifying the chromatogram produced. Detection of oxygenates is a further difficulty due to their often very low response in both ECD and FID. Use of elemental specific detection such as AED offers

some potential in atmospheric oxygenate analysis although AED sensitivity for oxygen is only around 100 pg s^{-1}. Detectors such as the helium ionization detector (HID), which produce a nonselective high sensitivity response to these types of compounds, may in future allow on-line measurements of oxygenates with GC, assuming sufficient chromatographic resolution or trapping selectivity can be obtained.

Future Work

Gas chromatography has an important role to play in monitoring mankind's emissions into the atmosphere and exploring the natural balance of biogenically released materials. New developments in injection technology and adsorbent materials will allow a greater number of species to be determined automatically in field locations. Development in column technology to reduce the effect of moisture on chromatographic separation and broaden the range of volatilities that may be separated on a given column will also bring significant benefits. Improvements in detector sensitivities and reliability (notably bench-top MS) will determine which of the many available detectors become standard in the next generation of atmospheric instruments.

See Colour Plates 56, 57, 58.

See also: **II/Chromatography: Gas:** Detectors: General (Flame Ionization Detectors and Thermal Conductivity Detectors); Detectors: Mass Spectrometry; Detectors: Selective. **III/Environmental Applications:** Gas Chromatography-Mass Spectrometry.

Further Reading

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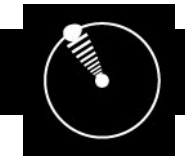
BACTERIOPHAGES: SEPARATION OF



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Introduction

Bacteriophages are viruses that infect bacteria. Historically, interest in bacteriophages was first generated by the possibility of using bacteriophages as biological antibiotics. This interest is periodically revived when difficulties are encountered with the use of chemical antibiotics. Interest in bacteriophages was also generated by both the short life cycle and the simple (short) genome of bacteriophages. These characteristics were useful in developing the science of molecular genetics. Bacteriophages were a favourite